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Low-pressure non-equilibrium plasma technologies – scientific background and technological challenges

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Non-equilibrium gaseous plasma is a medium suitable for tailoring surface properties of solid materials. It contains free electrons, positively charged ions, molecular radicals, electronically excited atoms and molecules, and vibrationally excited molecules. The neutral gaseous species are usually at room or somehow elevated temperatures, and the electrons are at the temperature of a few 10,000 K. The electrons are retarded by the negative surface potential, and positively charged ions are accelerated so they reach the surface with a kinetic energy of about 10 eV, less if they collide within the sheath between plasma and solid material. The electrons from the high-energy tail of their distribution are capable of exciting gaseous molecules and atoms to energetic levels, and the relaxation of these levels by dipole radiation is the source of photons. The radiation in the vacuum ultraviolet range often prevails.

The surface modification of solid materials is a consequence of the interaction between plasma species and the surface film of solid materials. Plasma species of high potential and/or kinetic energy interact chemically with solid materials. The effect of ions and radicals is often limited to a very thin surface film (unless the material is additionally biased and thus treated with energetic ions), while the photons penetrate deeper into the solid materials, depending on the structure and the photon energy. Vacuum ultraviolet radiation is usually absorbed in a film whose thickness is of the order of 10 nm. The surface reactions may trigger modifications that propagate deeper into the material, sometimes well after accomplishing the plasma treatment.

The intensity of surface reactions depends on the surface temperature and the flux of plasma species onto the surface. The complete knowledge about surface kinetics requires knowledge of the fluxes and the surface composition/structure versus the treatment time. The fluxes are rarely reported in scientific literature. Instead, the literature reports external parameters such as the peculiarities of the plasma reactor, the gas pressure and flow rates, the type of discharge and discharge coupling, the power of the plasma generator, the treatment time and alike. Such an incomplete plasma characterization makes the results of the surface finish reported in different scientific documents incomparable. Reviewing scientific literature often shows little correlation (if any) between the external (discharge) parameters and the surface finish. Furthermore, it makes upscaling difficult since the fluxes of reactive species follow unknown dependence on the external parameters. Namely, the fluxes often drift with treatment time unpredictably because of numerous effects, including the irreversible changes in the surface properties of materials facing plasma, changes in the plasma composition and, thus, plasma parameters, and thermal effects since most surface reactions are exothermic. A scientific challenge is drawing correlations between the surface modifications and the fluxes of plasma species.

Once the correlation is known, the upscaling to industrial treatment is solely a technological challenge. An appropriate choice of the reactive gas and gas pressure should enable a similar flux in a large industrial reactor as previously found suitable in a small experimental reactor, providing the discharge coupling enables similar plasma parameters. Coupling powerful plasma generators to sustain uniform plasma in large reactors is a technological challenge because of numerous effects that are marginal in experimental reactors. Plasma uniformity is impossible to achieve in reactors of the volume of the order of cubic meter, so the appropriate surface finish should be achieved in a range of fluxes large enough to compensate for plasma non-uniformity. Lowering the pressure in the plasma reactor usually improves plasma uniformity but at the expense of the smaller fluxes of plasma species. The selection of the gas pressure is thus usually a compromise between plasma uniformity and the flux of plasma species.

Many technologies require small doses of plasma species. For example, surface functionalization with desired functional groups is often accomplished after receiving the dose of radicals between about 10^{20} and 10^{22} m^{-2}, so the treatment may last a second or less. Over-treatment is often as bad as insufficient treatment because of numerous detrimental effects that are observed at large doses of plasma species. On the other hand, the deposition of thin films and (selective) etching may require large doses of plasma species, sometimes exceeding 10^{25} m^{-2}. Such large doses are only achievable after prolonged treatment of solid materials with gaseous plasma. Regardless of the pressure of the reactive gas or the normalized discharge pressure, the flux of reactive plasma species is often limited to about 10^{23} $m^{-2}s^{-1}$ in low-temperature nonequilibrium gaseous plasma sustained in reactive gases. While treatment of materials with smooth surfaces can usually be accomplished in a time scale of seconds or minutes, powders should be treated for longer times because of the large surface-to-volume ratio. Another factor that limits the achievable treatment time is the formation of dusty plasma, i.e., gas-phase synthesis of small particles whose size increases with the treatment time. Pulsed discharges will limit this effect.